Rec'd PCT/PTO 29 APR 2005

REC'D 09 FEB 2005
WIPO PCT

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference TS 1320 PCT	**FOR FURTHER ACTION**	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/EP 03/50765	International filing date *(day/month/year)* 29.10.2003	Priority date *(day/month/year)* 29.10.2002
International Patent Classification (IPC) or both national classification and IPC C10L3/06		
Applicant SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ..et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.

2. This REPORT consists of a total of 6 sheets, including this cover sheet.

   ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

   These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

   - I ☒ Basis of the opinion
   - II ☐ Priority
   - III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
   - IV ☐ Lack of unity of invention
   - V ☒ Reasoned statement under Rule 66.2(a)(ii) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
   - VI ☐ Certain documents cited
   - VII ☐ Certain defects in the international application
   - VIII ☐ Certain observations on the international application

Date of submission of the demand	Date of completion of this report
25.05.2004	08.02.2005
Name and mailing address of the international preliminary examining authority: European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized Officer Deurinck, P Telephone No. +31 70 340-2404

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/EP 03/50765

I. Basis of the report

1. With regard to the **elements** of the international application *(Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17))*:

Description, Pages

1-10, 12, 13	as originally filed
11	received on 23.11.2004 with letter of 22.11.2004

Claims, Numbers

1-13	filed with telefax on 21.01.2005

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

   These elements were available or furnished to this Authority in the following language: , which is:

   ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).

   ☐ the language of publication of the international application (under Rule 48.3(b)).

   ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

   ☐ contained in the international application in written form.

   ☐ filed together with the international application in computer readable form.

   ☐ furnished subsequently to this Authority in written form.

   ☐ furnished subsequently to this Authority in computer readable form.

   ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.

   ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

   ☐ the description, pages:

   ☐ the claims, Nos.:

   ☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).

   (Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-6,9,11
	No:	Claims	7,8,10,13
Inventive step (IS)	Yes:	Claims	1-6,12
	No:	Claims	7,8,9,10,11,13
Industrial applicability (IA)	Yes:	Claims	1-13
	No:	Claims	

2. Citations and explanations

see separate sheet

Re Item V

Reasoned statement with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

Reference is made to the following documents:

D1: US 3 725 299
D2: US 5 041 693
D3: EP 0 335 034
D4: US 3 051 646
D5: US 3 566 611
D6: GB 2 275 625
D7: US 4 358 297
D8: US 3 188 293
D9: WO 00/56441
D10: CN 1227255 (abstract)

1. Novelty

1.1

The present application meets the criteria of Article 33(1) PCT, because the subject-matter of independent **Claim 1** is new in the sense of Article 33(2) PCT.

None of the prior art documents discloses a process for the removal of sulphur compounds from a hydrocarbon stream comprising

- contacting said hydrocarbon stream with an adsorbent; and
- regenerating said loaded adsorbent with a regeneration gas stream *containing a certain amount of water.*

1.2

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of independent **Claim 7** is not new in the sense of Article 33(2) PCT.

Document D1 discloses a process for the regeneration of adsorbent comprising a zeolite having a pore diameter of at least 5 Å by contacting the adsorbent with a regeneration

gas stream having a relative water humidity less than 100%, suitable for a period up till 12 hours (see D1: claim 1; column 1, lines 5-13; column 5, line 11).

Similar novelty objections can be made based on documents D2 (claim 1; column 8, lines 59-64), D3 (claims 11 and 17; page 6, lines 37-56), D4 (column 2, lines 29-68; column 3, lines 37-59, claim 1), D5 (column 3, lines 21-38; column 4, lines 29-59; claim 1), D6 (page 2, lines 6-8; page 4, lines 12-18; claim 1), D7 (column 4, lines 18-52; claim 1), D8 (claims 1 and 2), D9 (page 6, lines 14-26; page 7, lines 12-21; claim 1) and D10 (see abstract).

1.3
The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of independent **Claim 13** is not new in the sense of Article 33(2) PCT.

Document D7 discloses a process for reducing the degradation of a sulphur loaded adsorbent (see D7: column 4, lines 12-17), wherein the sulphur loaded adsorbent is regenerated in the presence of water (see D7: column 7, lines 55-57) by contacting said loaded adsorbent with a regeneration gas stream having a relative humidity less than 100%, wherein the regeneration gas stream is an inert gas (see D7: column 4, lines 49-52).

1.4
The following dependent Claims are also not new:
- **Claim 8**: D3: page 10, lines 1-8;
- **Claim 10**: D3: page 6, lines 7-56 and page 10, lines 9-13; D4: column 4, lines 19-34;

2. Inventive Step

2.1
The present application meets the criteria of Article 33(1) PCT, because the subject-matter of independent **Claim 1** involves an inventive step in the sense of Article 33(3) PCT.

Document D1, which is considered to represent the most relevant state of the art, discloses a process for the removal of sulphur compounds from natural gas condensates, comprising

- contacting said feed stream with an adsorbent comprising a zeolite having a pore diameter of at least 5 Å; and
- regenerating said loaded adsorbent by contacting with a low boiling readily condensible paraffin desorbent in the vapour phase (see D1: claim 1; column 1, lines 5-13; column 2, lines 34-48).

The subject-matter of Claim 1 differs from D1 in that the regeneration gas is an inert gas containing a certain amount of water (*distinguishing feature*), whereas in D1 no water is present in the regeneration gas stream and the regeneration gas stream is not an inert gas.

The technical effect that might be achieved with this distinguishing feature is to increase the adsorbent lifetime (see description pages 12 and 13; letter of applicant dated 22/11/2004).

The problem to be solved by the present invention may be regarded as: "To provide an improved process with a substantial reduction in degradation of the adsorbent without the need for additional and cumbersome steps".

Starting from the disclosure of D1 and intending to solve the above-mentioned problem, a person skilled in the art had no incentive from the state of the art to use a inert gas stream containing a certain amount of water as the regeneration gas stream.

Thus the subject-matter of independent Claim 1 involves an inventive step.

2.2

There is no evidence on file that the additional technical features of dependent **Claims 9 and 11** might cause a technical effect. Consequently, it cannot be seen which technical problem is solved. Therefore, an inventive step cannot be acknowledged.

preferably 50 - 90 bara, a temperature between 200 and 400 °C, preferably between 230 and 350 °C, and a superficial gas velocity of less than 0.20 m/s, preferably between 0.02 and 0.15 m/s. The regeneration gas stream to be used may be in principle each inert gas or inert gas mixture. Suitably nitrogen, hydrogen or a hydrocarbon gas stream is used, preferably a treated gas stream which obtained by a sulphur removal process as described above. The regeneration gas stream having a certain relative water humidity to be used in any of the above-described process may be obtained by any suitable method. For instance, a dry gas may be mixed with a saturated gas, or a dry gas stream is saturated followed by an increase of the temperature. Preferably the regeneration gas stream is a gas stream obtained by saturating the stream at a temperature below the regeneration temperature, preferably at least 50 °C below the regeneration temperature, more preferably 75 °C below the regeneration temperature, followed by heating the stream till the regeneration temperature.

The relative humidity of the regeneration gas stream is suitably at least 0.1%, more suitably at least 4%. Preferably the regeneration gas stream is a gas stream having a relative humidity between 5 and 60%, preferably between 10 and 30%. The combination of a relative humidity of between 5 and 6, preferably between 10 and 30% is especially preferred in combination with a temperature between 200 and 400 °C, preferably between 230 and 350 °C and a pressure between 30 and 120 bara, preferably between 50 and 90 bara.

CLAIMS

1. A process for the removal of sulphur compounds from a hydrocarbon stream, especially a gaseous hydrocarbon gas stream, comprising said sulphur compounds, which process comprises contacting said gas stream with an adsorbent comprising a zeolite having a pore diameter of at least 5 Å to adsorb the sulphur compounds thereon, the adsorption process followed by a regeneration process of used, loaded adsorbent by contacting the said loaded adsorbent with a regeneration gas stream having a relative water humidity less than 100%, especially less than 80%.

2. A process according to claim 1, in which the hydrocarbon stream is natural gas, associated gas, a natural gas liquids stream, a natural gas condensate stream or a refinery gas stream.

3. A process according to claim 1 or 2, in which the sulphur compounds are hydrogen sulphide, carbonyl sulphide, mercaptans, especially C_1-C_6 mercaptans, organic sulphides, especially di-C_1-C_4-alkyl sulphides, organic disulphides, especially di-C_1-C_4-alkyl disulphides, thiophene compounds, aromatic mercaptans, especially phenyl mercaptan, or mixtures thereof, preferably mercaptans, more especially C_1-C_4 mercaptans, the total amount of sulphur compounds preferably being up to 3 vol% based on total gas stream, more preferably up till 1.5 vol%, more preferably up till 0.1 vol%, still more preferably between 1 and 700 ppmv, most preferably between 2 and 500 ppmv.

4. A process according to any of claims 1 to 3, in which the gas stream also comprises water, preferably is saturated with water, water preferably being removed before the removal of the sulphur compounds, more preferably by adsorbing the water on a zeolite having a pore diameter of less than 5 Å, even more preferably having a pore diameter of 3 or 4 Å.

5. A process according to any of claims 1 to 4, in which the gas stream also comprises hydrogen sulphide and optionally carbon dioxide, preferably up till 2 vol% hydrogen sulphide, more preferably up till 0.5 vol% hydrogen sulphide, the hydrogen sulphide and part of the carbon dioxide preferably being removed by means of washing the gas stream with a chemical and/or physical solvent, more preferably with an aqueous alkaline solution, even more preferably with an aqueous amine solution.

6. A process according to any of claims 1 to 5, in which the temperature of the zeolite adsorption process is between 10 and 60 °C, the pressure is between 10 and 150 bara, and the superficial gas velocity is between 0.03 and 0.6 m/s, preferably between 0.05 and 0.40 m/s.

7. A process for the regeneration of adsorbent comprising a zeolite having a pore diameter of at least 5 Å loaded with sulphur compounds by contacting the adsorbent with a regeneration gas stream having a relative water humidity less than 100%, especially less than 80%, suitably for a period up till 24 hours, preferably up till 12 hours.

8. A process according to any one of claims 1 to 7, in which the adsorbent comprises zeolite dispersed in a binder, preferably a molsieve, the zeolite preferably of zeolite type A or zeolite type X.

9. A process according to any of claims 1 to 8, in which the adsorbent is in the form of at least two beds, one bed comprising zeolite having a pore diameter of 5 Å, preferably 3 or 4 Å, the second and, if present, further beds comprising a zeolite having a pore diameter of more than 5 Å, preferably at least 6 Å, more preferably molsieve 13X.

10. A process according to any of claims 1 to 9, in which the regeneration is carried out at a pressure between 1 and 150 bara, a temperature between 200 and 400 °C, preferably between 230 and 350 °C, and a superficial gas velocity of less than 0.20 m/s, preferably between 0.02 and 0.15 m/s, the regeneration gas stream preferably being nitrogen, hydrogen or a hydrocarbon gas stream, more preferably a treated gas stream which is obtained by a process according to any of claims 1 to 9.

11. A process according to any of claims 1 to 10, in which the regeneration gas stream is a gas stream obtained by saturating the stream at a temperature below the regeneration temperature, preferably at least 50 °C below the regeneration temperature, more preferably 75 °C below the regeneration temperature.

12. A process according to any of claims 1 to 10, in which the regeneration gas stream has a relative humidity between 5 and 60%, more preferably between 10 and 30%.

REPLACED BY ART 34 AMDT